

## Module 1 : Atomic Structure

### Lecture 1 : Structural Chemistry

#### Objectives

In this Lecture you will learn the following

- The meaning of the terms molecular structure and geometry and electronic structure.
- Some interesting aspects of molecular structure through examples.
- Uncertainty principle.
- Principles of quantum mechanics, which provide a theoretical basis for structural chemistry.

#### 1.1 What do we mean by "Structure"?

By the word "structure" we refer to the process of visualizing an object as made up of parts and relating the parts to the entire object. The structure of a galaxy refers to its shape and the arrangement of the stars (and the planets therein) in the galaxy, the distances between them and so on. The structure of a galaxy is not static or frozen as the stars are moving with great speeds relative to one another. The structure of a building refers to its height, the number of floors, rooms, room sizes, the details of its foundation and so on. The structure of a solid material refers to the arrangement of atoms/molecules in the solid, the different types of arrangements and related details. Molecular geometry refers to the arrangement of the constituent atoms relative to one another. These atoms are not "fixed" but are constantly moving (rotating and vibrating) relative to each other.

Atoms and molecules contain electrons and the "structure" or the arrangement of electrons in these is referred to as the electronic structure. You may recall that the electronic configuration of a lithium atom is  $1s^2 2s^1$ . This is only one aspect of the electronic structure of an atom. To describe molecular structure, in addition to the electronic configuration, we have to identify its vibrational and rotational structure. Since electrons and nuclei are not stationary objects, their structure is inherently associated with the dynamical behaviour of these "objects".

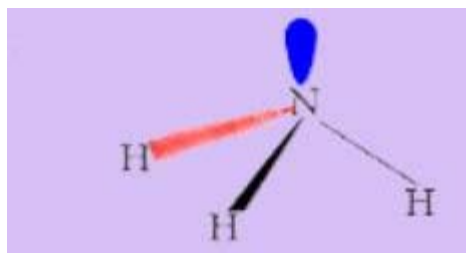
In this introductory chapter, we will give examples of several interesting structures in chemistry, describe in brief their technological applications and prepare the groundwork for the necessity of using connotation for understanding the microscopic structure of matter.

#### 1.2 Example of molecular structures

The examples of structures considered here are structure of ammonia and its inversion, D / L configurations of molecules,  $C_{60}$  with an included atom, a micelle and a protein.

##### The structure of ammonia

Ammonia has a pyramidal structure with nitrogen at its apex and the three hydrogens at the base. The HNH angle is  $107.3^\circ$  close to the tetrahedral angle of  $109^\circ 28'$ . The lone pair of electrons is situated above the N atom and away from the H-atoms. An interesting feature of this structure is that the N atom can go back and forth through the triangle formed by the three hydrogens to the other side of the triangle. This is referred to as umbrella inversion or "tunneling". The action of the ammonia maser is based on this phenomenon.



**Figure 1.1 Ammonia**

### D and L Glyceraldehydes

A carbon atom bonded to four distinct groups is referred to as an asymmetric or a chiral carbon atom. One simple example of a molecule containing an asymmetric carbon atom is d glyceraldehyde, shown in Fig 1.2. The mirror image of D glyceraldehyde, L glyceraldehyde is also shown. In the figure, H and OH groups are above the plane of paper and the CHO and CH<sub>2</sub>OH groups are below the plane of the paper. By rotating D glyceraldehyde with respect to any axis, it cannot be converted to L glyceraldehyde. (Try this using molecular models). This is similar to a person having a mole on his left cheek. In the mirror, the mole appears on his right cheek. If one rotates the person by 180°, the mole still remains on the left cheek and the rotated person differs from the mirror image.

If you look at the carbon center, with the hydrogen atom further away from it, the groups CHO, CH<sub>2</sub>OH and OH which are nearer to the eye than the H atom, are arranged clockwise. In the L configuration, they are arranged counterclockwise. These asymmetric molecules rotates the plane of polarization of a plane polarized light. The configuration of molecules are critical, e.g. a molecule can act as a drug only in one of the two configurations (not the always). Naturally occurring amino acids have L configurations.

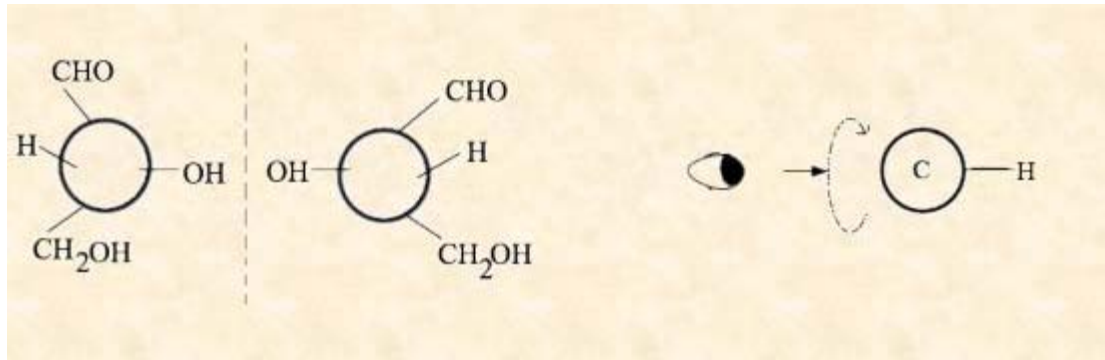


Figure 1.2 D and L Glyceraldehydes. The left part of the figure has a mirror plane separating D and L glyceraldehydes. The right part shows the rotation of the molecule with respect to the C-H bond when the bond is directed away from the eye.

### 1.3 The Structure of C<sub>60</sub>

Carbon is well known to exist in the forms of graphite and diamond. In graphite, the atoms are arranged in a plane, with each atom connecting three other atoms. Adjacent planes are held together by weak interactions (which are much weaker than covalent or ionic interactions). The planes can slide against each other. That is why graphite is used in pencil. In diamond, the atoms are tetrahedrally linked to one another to form a strongly knit three dimensional network. Another allotrope of carbon was discovered in the nineties. This form, buckminsterfullerene (C<sub>60</sub>) has sixty atoms lying approximately on the surface of a sphere. The structure is shown in Fig 1.3. Other forms such as C<sub>70</sub> have also been discovered. These units can be packed to form molecular solids.

In Fig 1.3, a C<sub>60</sub> which has enclosed a potassium has been shown. This is an example of an ion or a small molecule encased in a larger molecule. The process of encasing is useful for transporting small molecules across membranes or regions wherein direct transport is chemically unfeasible.

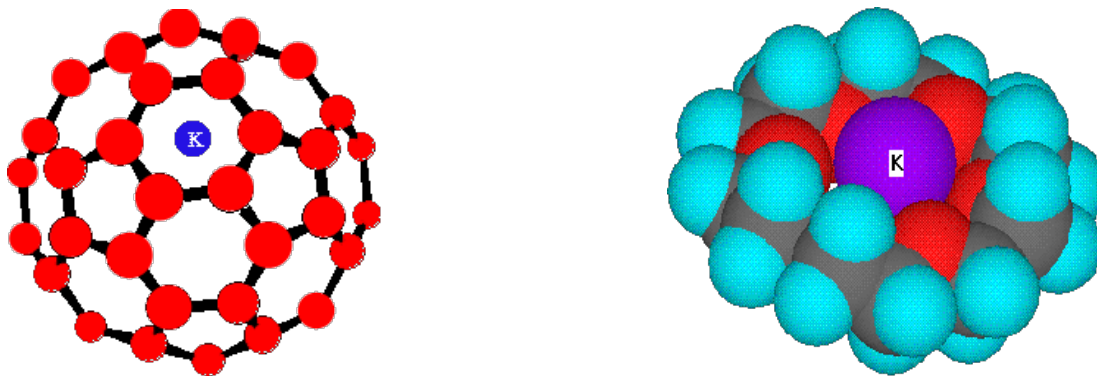


Figure 1.3: Structure of  $C_{60}$  which has enclosed a potassium ion

#### 1.4 The structure of Micelle.

Chain molecules such as soap contain hydrophilic (water loving) groups like  $SO_3H$  at one end and hydrophobic (water repelling) groups like alkyl groups at the other end. At very low concentrations they do not dissolve in water. Above a concentration called the critical micelle concentration (cmc) the solubility abruptly increases due to the formation of micelles. In a micelle, the hydrophobic groups come together forming a core and hydrophilic groups (which are either charged or dipolar in nature) which are outward are in contact with water molecules. An example of such a structure formed by cetyl trimethyl ammonium bromide (CTAB) is shown in Fig 1.4. It is seen that in the centre of the micelle, a hydrophobic entity has been trapped. Some water molecules which are trapped in the micelle are also shown.

The interior of a micelle is like an oil drop. Micelles can be of various shapes. Micelles are used as detergents and drug carriers and find applications in froth flotation and petroleum recovery. In the action of a detergent, the dust particle to be removed is carried away in the hydrocarbon interior (hydrophobic) of a micelle.

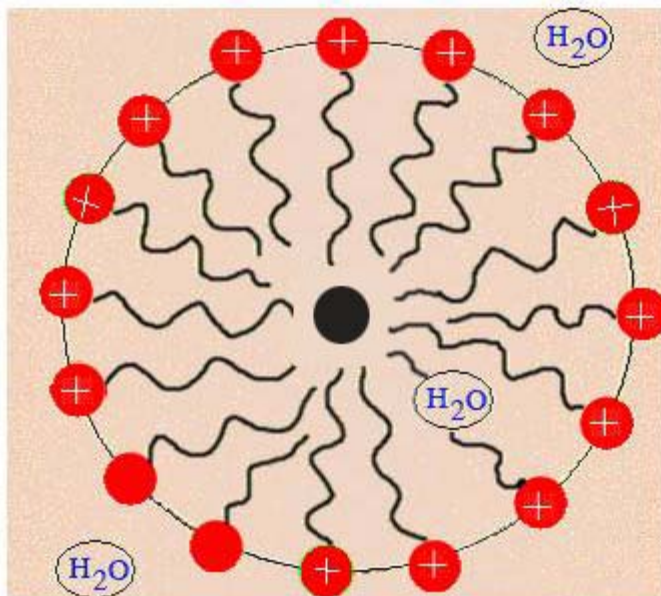


Figure 1.4: Micelle formed by cetyl trimethyl ammonium bromide (CTAB).

#### 1.5 The Structure of Insulin

Fig 1.5 shows the structure of the protein insulin which helps in carbohydrate metabolism and stimulates protein synthesis. A protein consists of a sequence of polypeptide chains. The building blocks are amino acids which contain an amino group ( $NH_2$ ,  $NH$ ) and a carboxylic acid group ( $-COOH$ ). There are 20 amino acids commonly found in proteins. The amino acids can form polypeptide chains when an  $NH_2$  group of one amino acid combines with the  $COOH$  group of an adjacent amino acid by forming an amide linkage  $-CO-NH$  by eliminating a water molecule. Proteins constitute a complex class of macromolecules exhibiting versatile structures and they are

fundamental to biology since they are the instruments through which genetic information is expressed. The sequence (of the covalent linkages through amide bonds) of amino acids forms the primary structure of protein. The geometrical arrangements of polypeptide chains along their axis constitute their secondary structure. (e.g., helical structures)

The tertiary structure refers to the packing of the primary and secondary structural units in three dimensions. Many globular (spherical) proteins having a molecular weight greater than 50000 consist of two or more polypeptide chains (oligomers). Quaternary structure refers to the native conformation of an oligomeric protein in which different polypeptide chains fit relative to one another. Bovine insulin consists of two chains of amino acids. (A chain with 21 amino acids and B chain of 30 amino acids). There are two disulphide (-S-S-) bonds that connect to A and B chains one at 7<sup>th</sup> amino acid of A chain and the 7<sup>th</sup> amino acid of another and the second disulphide bond between the 20<sup>th</sup> amino acid of A and 19<sup>th</sup> amino acid of B. There is an additional disulphide bond between the 6<sup>th</sup> and 11<sup>th</sup> amino acid of chain A. The structure of insulin is shown in Fig. 1.5.

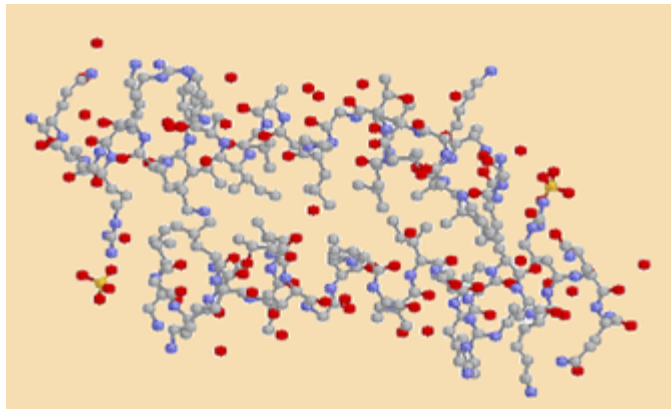


Figure 1.5 The Structure of Insulin dimer and

hexamer

After looking at the previous structures, two questions are automatic. How are these determined? What is the theoretical basis of understanding these structures? The experimental basis is spectroscopy, which will be discussed in later chapters. We turn to the theoretical basis first. From the theoretical basis which is given by quantum mechanism, all the above structures can be "derived" or understood.

### Electronic structure

With electronic structure we cannot associate "geometries" such as molecular geometry or geometrical arrangements corresponding to other objects. Electrons are neither point objects nor stationary objects. Associated with a "stable" arrangement of electrons around one or more nuclei are

- a) a set of discrete energy levels.
- b) an electronic configuration resulting from the occupation of electrons in these energy levels.
- c) an electronic charge density which can be measured experimentally.
- d) an energy spectrum resulting from the transitions between these levels.

By electronic structure, we mean all of a), b), c) and d) above and this will be illustrated in the next few chapters.

### 1.6 Foundations of Quantum Theory

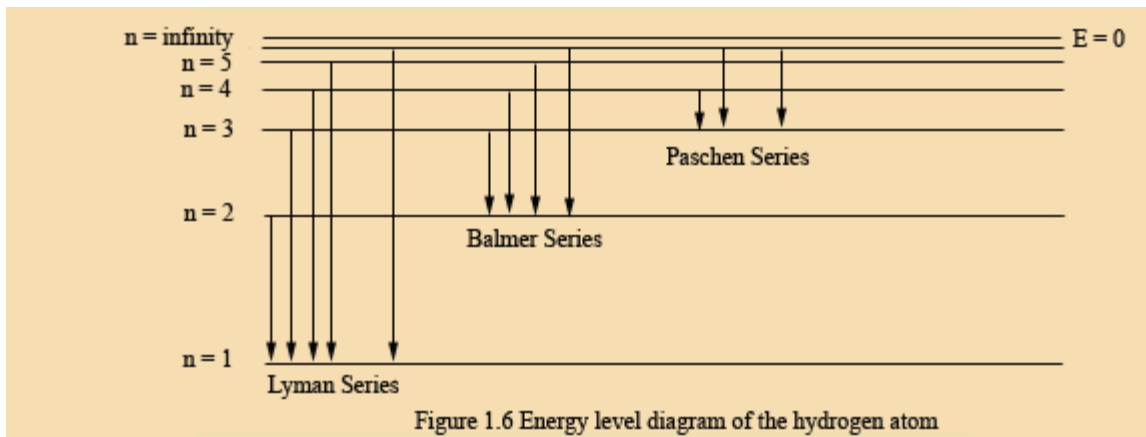
Bohr attempted to explain atomic structure by certain postulates, which deviated in several ways from the classical or Newtonian mechanics. In Newtonian mechanics, the position and the momentum (or the velocity) of the particle (or a collection of particles) can be simultaneously determined at each instance of time. By an analogy to the orbits of planets in planetary motion, Bohr postulated that an electron of an atom exists in "stationary" states in these orbits, which he assumed to be circular.

Since this postulate alone was not sufficient to explain the spectral lines obtained by Balmer, Lyman, Paschen and others, he further postulated that the angular momentum of the electron in these orbits ( given by  $mvr$ , where  $m$  is the electron mass,  $v$ , its velocity and  $r$ , its radius in the circular orbit) was quantized and was equal to  $n\hbar$  where  $\hbar = h/2\pi$  with  $h = \text{Planck's constant} = 6.626 \times 10^{-34} \text{ Js}$ , and  $n$  can take on only integer values. Whenever the atom absorbed an energy  $E$  which was equal to the difference of energy between any two levels of the atom, there was a change of state of the atom from one stationary state to another stationary state. Using these postulates, the following formula for the energy difference between the two levels can be easily derived.

$$E_2 - E_1 = -R_H \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right) \quad (1.1)$$

where  $R_H = 109737 \text{ cm}^{-1}$  is called the Rydberg constant and  $E_2$  and  $E_1$  are the energy levels of the second and the first stationary state, respectively.

Using this formula, Bohr could obtain all the lines of the spectrum of H-atom which is shown in the Figure 1.6.



While this theory explained the structure of the hydrogen atom well, it could not explain the structures of other atoms and molecules.

### 1.7 The Uncertainty Principle

In the newer and more accurate theory of matter given by Heisenberg, Schrödinger and Dirac, the description of matter is not based on the simultaneous specification of positions and momenta of particles. This implies that we cannot speak of the trajectories of these subatomic particles at all. Indeed, the Heisenberg uncertainty principle states that the position and the momentum of a particle cannot be determined simultaneously and the product of the uncertainty of the position  $\Delta x$  and the uncertainty of momentum  $\Delta p_x$  is given by

$$\Delta x \Delta p_x \geq \hbar \tag{1.2}$$

Here the motion has been considered only in the x-direction.

There is thus a fundamental difference in the description of observables such as position, momentum and even others such as energy. The uncertainty in position is akin to the error in measuring the position and can be taken as the root mean square deviation in the position of the particle which is given by

$$[\langle x^2 \rangle - \langle x \rangle^2]^{1/2}$$

where the angular brackets  $\langle \rangle$  refer to the average values.

The new description of matter can be formulated in terms of postulates or laws, which will replace Newton's laws. The new description goes over to or becomes equivalent to the classical description when the particle size is "macroscopic", e.g., 0.01g or greater in mass. These postulates are summarized in the next paragraph. You may wonder about the justification of these seemingly strange postulates. The final justification is the agreement of the results of the theory with experiments. We are forced to seek these and other newer descriptions whenever old laws such as Newton's laws fail to explain phenomena involving electrons, atoms and molecules and other microscopic objects such as protons, neutrons, photons and so on. If the new description fails to explain all the observed phenomena, we have no choice but to replace the new postulates by more appropriate laws as and when they are discovered. It turns out that with the present postulates, a fairly accurate description of molecular structures can be obtained.

The dynamical variables (which characterize and describe the motion of an object) such as position, momentum, angular momentum and energy are replaced by "operators". These operators operate on functions. When these operators operate on functions, new functions may result. However, in special cases, the result may be the original function multiplied by a constant. As an example, consider the operator  $d/dx$  ( the derivative operator) and functions  $\sin(ax)$  and  $\exp(ax)$ . The result of operating the operator on the two functions is shown below.

$$\frac{d}{dx} \sin(ax) = a \cos(ax) \tag{1.3}$$

$$\frac{d}{dx} \exp(ax) = a \exp(ax) \quad (1.4)$$

In the second example, we get a constant multiplied by the original function. The function  $\exp(ax)$  is called an eigenfunction of the operator  $d/dx$  with an eigenvalue  $a$ . The function  $\sin(ax)$  is not an eigenfunction of  $d/dx$  because on operating on the function by the operator  $d/dx$ , we do not get a constant multiplied by the same function. An understanding of atomic and molecular structure and dynamics is based on the successful application of the following postulates.

1) The dynamical variables are replaced by operators. e.g.,

a) Position  $x$  replaced by  $x$ .

b)  $x$ -component of momentum  $p_x$  replaced by  $\left(\frac{\hbar}{i}\right) \frac{\partial}{\partial x}$  where  $i = \sqrt{-1}$

c)  $x$  component of kinetic energy  $p_x^2 / 2m$  replaced by  $-\left(\frac{\hbar^2}{2m}\right) \frac{\partial^2}{\partial x^2}$  where  $m$  is the mass of the particle.

2) Experimental observations on the dynamical variables yield the eigenvalues of the corresponding dynamical variables. When the energy of a system (atom, molecule or a cluster of molecules) is measured, the result will be an eigenvalue of the energy operator.

3) All the possible microscopic information of the system can be obtained from the wavefunction of the system which is a solution of the Schrödinger equation.

$H\Psi = E\Psi$ , where  $H$  is the operator for the total energy of the system. The energy of the system is a sum of the kinetic energies of all the particles and the potential energy of interaction between all the particles.  $\Psi$  (which is called the wavefunction) is a function of the coordinates of all the particles of the system.

4) The probability of finding a particle in a given volume element ( $d\tau$ ) of space is given by  $|\Psi|^2 d\tau$ , where  $|\Psi|$  denotes the absolute value of  $\Psi$

## 1.8 Problems

1.1) Distinguish between the structures of trees, buildings, bridges, the earth and the nucleus of an atom. Identify the building blocks and the forces that bind them.

1.2) The angular momentum  $\mathbf{L}$  of a particle is given by  $\mathbf{r} \times \mathbf{p}$  where  $\mathbf{r}$  and  $\mathbf{p}$  are position and momentum vectors respectively. The  $x$  component of angular momentum  $L_x$  equals  $y p_z - z p_y$ . What is the operator for  $L_x$ ? (Hint: The operator for the sum of two dynamical variables is the sum of the operators for the dynamical variables.)

1.3) What is the energy required to excite 1 mole of hydrogen atoms from the  $n = 2$  state to the  $n = 7$  state? Express the values of energy in eV, kJ, kJ/mol and  $\text{cm}^{-1}$ .

## Recap

In this lecture you have learnt the following

### Summary

In this lecture we have quantified the meaning of electronic structure and contrasted it with structures and geometries of a few interesting molecules. These geometries include  $\text{NH}_3$ , D/L isomers of an optically active compound, a potassium ion trapped inside a  $\text{C}_{60}$ , a protein molecule and a micellar aggregate. Electronic structure was associated with an energy level diagram with electrons "occupying the lower levels, a charge density of electrons associated with these levels and a spectrum which is a signature of these levels. Quantum theory began with the works of Planck (who gave the formula  $E = nh\nu$ ), where  $\nu$  is the frequency of light and  $n$  = number of photons. It was further developed by Bohr, Heisenberg, Schrödinger and Dirac.

# **Module 1 Electronic Structure and Covalent Bonding**

## **Lecture 1 Structure and Bonding I**

### ***1.1 The Structure of an Atom***

An atom consists of a tiny dense nucleus surrounded by electrons. The nucleus contains positively charged protons and neutral neutrons. A neutral atom has an equal number of protons and electrons. Atoms can gain electrons and thereby become negatively charged, or they can lose electrons and become positively charged. However, there won't be any change in the number of protons. Most of the mass of an atom is in its nucleus and most of the volume of an atom is occupied by its electrons. The atomic number of an atom equals to the number of protons and the number of electrons. The mass number of an atom is the sum of its protons and neutrons. The number of neutrons of an atom can be varied, so an atom can have different mass number.

### ***1.2 The Distribution of Electrons in an Atom***

The electrons are the greatest importance in organic chemistry. A neutral atom of each element contains an equal number of protons and electrons. According to quantum mechanics, the electrons in an atom can be thought of as occupying a set of shells. The first shell is the closest to the nucleus and subsequent shells lies farther from the nucleus. Each shell contains subshells known as atomic orbitals that have a characteristic shape and energy. They occupy a characteristic volume of the space. The atomic orbital that is close to the nucleus, is lower in its energy.

The first shell consists of only *s* atomic orbital. The second shell consists of *s* and three degenerate *p* atomic orbitals and the third shell contains, in addition, five degenerate *d* atomic orbitals. The fourth and higher shells contain, in addition, seven degenerate *f* atomic orbitals. Degenerate orbitals are orbitals that have the same energy. Each atomic orbital can have maximum of two electrons. There are only two electrons in the first shell as it has only *s* atomic orbitals. The second shell can have a total of eight electrons for one *s* and three *p* atomic orbitals. The third shell has nine atomic orbitals, one *s*, three *p*, and five *d* atomic orbitals, so eighteen electrons can occupy these nine atomic orbitals. Thirty two electrons can be occupied by the sixteen atomic orbitals of the fourth shell. When the electrons are in the available orbitals with the lowest energy, we call it as the



ground-state electronic configuration of the atom. One or more electrons can jump into a higher energy orbital, if energy is applied to the atom in the ground state. We call it as an excited-state electronic configuration.

The following principles are used to determine which orbitals occupy the electrons:

- According to the **aufbau principle**, an electron always goes into the available lower energy orbital. The relative energies of the atomic orbitals follow:

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f$$

$1s$  atomic orbital is closer to the nucleus and lower in energy than  $2s$  atomic orbital, which is lower in energy and closer to the nucleus than  $3s$  atomic orbital. While comparing atomic orbitals in the same shell,  $s$  atomic orbital is lower in energy than  $p$  atomic orbital, and  $p$  atomic orbital is lower in energy than  $d$  atomic orbital.

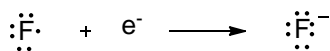
- According to the **Pauli Exclusion Principle**, only two electrons can occupy each atomic orbital, and the two electrons must be of opposite spin. The single electron of a hydrogen atom occupies  $1s$  atomic orbital, the second electron of a helium atom fills the  $1s$  atomic orbital, the third electron of a lithium atom occupies  $2s$  atomic orbital, the fourth electron of a beryllium atom fills the  $2s$  atomic orbital. The fifth electron of a boron atom occupies any one of the three degenerate  $2p$  atomic orbitals.
- According to the **Hund's rule**, when there are degenerate orbitals, an electron will occupy an empty orbital before it starts to pair up.

### ***1.3 Ionic, Covalent and Polar Bonds***

According to Lewis's theory, an atom is most stable if its outer shell is either filled or contains eight electrons. So it will give up, accept, or share electrons in order to achieve a filled outer shell or an outer shell that contains eight electrons. This theory is called as **octet rule**. Lithium (Li) has a single electron in its 2s atomic orbital. The lithium atom ends up with a filled outer shell, a stable configuration, if it loses the 2s electron.

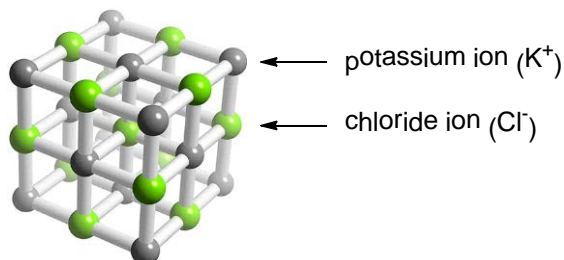
Energy released on removing an electron from an atom is called **ionization energy**. Lithium has relatively low ionization energy because loss of electron leads to stable configuration and become a positively charged. The elements in the first column of the periodic table, alkali metals, are all electropositive because they lose their outermost electron readily. Electrons in inner shells, called core electrons, do not participate in chemical bonding. Electrons in the outermost shell are called **valence electrons**, and the outermost shell is called the valence shell. Carbon, for example, has two core electrons and four valence electrons.

The chemical behavior of an element depends on its electronic configuration. Elements in the same column of the periodic table have the same number of valence electrons, and have similar chemical properties. When we draw the electrons around an atom, only valence electrons are shown as a dot. Sodium readily loses its valence electron to have stable electronic configuration and becomes positive ion. Fluorine gains one electron to achieve stable electronic configuration and becomes negative ion. Energy is released when an atom gains an electron.



### 1.3.1 The Ionic Bond

A chemical compound is called an ionic compound in which the components atoms exist as ions. Crystalline KCl results when potassium metal and chlorine gas are mixed. One electron is transferred from potassium atom to chlorine.

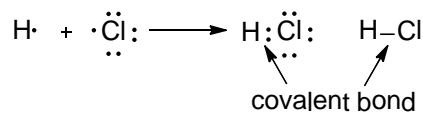
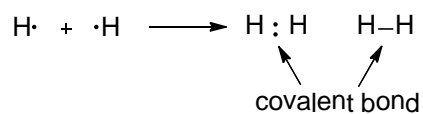


Crystal structure of KCl

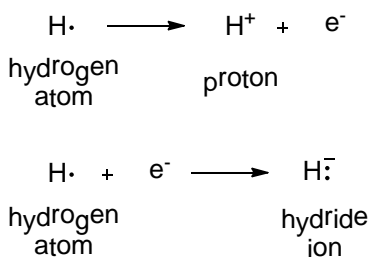
The positively charged potassium ions and negatively charged chloride ions are held together by the electrostatic attractions. An electrostatic attraction that holds ions together is called an **ionic bond**. Thus, the crystal structure of KCl is maintained by ionic bonds between potassium ions and chloride ions.

### 1.3.2 The Covalent Bond

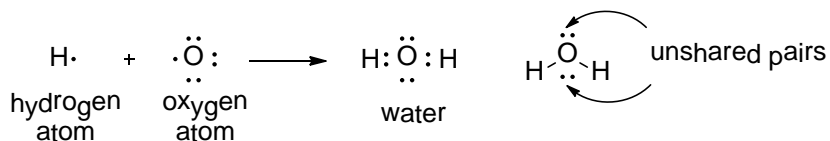
The covalent bond consists of an electron pair that is shared between bonded atoms instead of giving up or gaining electrons. Two hydrogen atoms can form a covalent bond by sharing electrons. As a result of covalent bonding, each hydrogen acquires a stable, filled outer shell electronic configuration. Similarly, hydrogen and chlorine can form a covalent bond by sharing electrons.



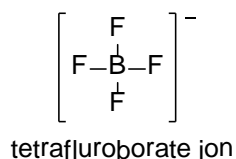
Molecular structures that use this notation for the electron pair bond are called **Lewis structures**. A hydrogen atom can achieve a completely empty shell by losing an electron and become a positively charged hydrogen ion, called proton. A hydrogen atom can achieve a filled outer shell by gaining an electron, thereby forming a negatively charged hydrogen ion, called hydride ion.



In some covalent compounds, however, some valence electrons remain unshared. For example, water (H<sub>2</sub>O) has six valence electrons. Two of these combine with hydrogens to make two O-H covalent bonds and four of the valence electrons remain unshared.



Ionic species such as [SO<sub>2</sub>]<sup>2-</sup>, [NH<sub>4</sub>]<sup>+</sup> and [BF<sub>4</sub>]<sup>-</sup> also contain covalent bonds. For an example, the tetrafluoroborate anion contains covalent B-F bonds.



The charge on each atom is called formal charge and the sum of the formal charges on the individual atoms must be equal to the total charge on the ion.

### 1.3.2 Polar Covalent Bonds

In many covalent bonds the electrons are not shared equally between two bonded atoms. For example, in hydrogen chloride the electrons are unevenly distributed between the two atoms because the atoms that share the electrons in the molecule are different and have different electronegativities. **Electronegativity** is the tendency of an atom to pull bonding electrons toward it. It increases as you go from left to right across a row of the periodic table or down to up in any of the columns. A bond in which electrons are shared unevenly is called a **polar bond** or **polar covalent bond**. A polar bond has a slight positive charge on one end and a slight negative charge on the other end. The greater the difference in electronegativity between the bonded atoms, the more polar the bond will be. The direction of bond polarity can be indicated with an arrow. The head of the arrow is at the negative end of the bond; a short perpendicular line near the tail of the arrow marks the positive end of the bond.



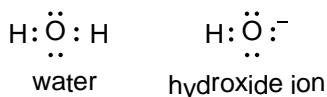
In this notation, the delta can be read as “partially” that indicates the hydrogen atom of HCl is “partially positive,” and the chlorine atom is “partially negative.” The uneven electron distribution in a compound containing covalent bonds is measured by a quantity called the **dipole moment** ( $\mu$ ). The dipole moment is commonly given in derived units called *debyes*, abbreviated D. The dipole moment is defined by the following equation:

$$\mu = qr$$

In this equation,  $q$  is the magnitude of the separated charge and  $r$  is a vector from the side of positive charge to the site of negative charge. For example, the HCl molecule has a dipole moment of 1.08 D. Molecules that have permanent dipole moments are called polar molecules. Some molecules contain several polar bonds. In such case, each polar bond has associated with it's a dipole moment contribution, called a **bond dipole**. The net dipole moment of such a polar molecule is the vector sum of its bond dipoles. Carbon dioxide molecule is not a polar molecule, even though it has polar bonds. Carbon dioxide is linear, and the C-O bond dipoles are oriented in opposite directions. So they cancel out each other and the dipole moment is zero.

## 1.4 Representation of Structure

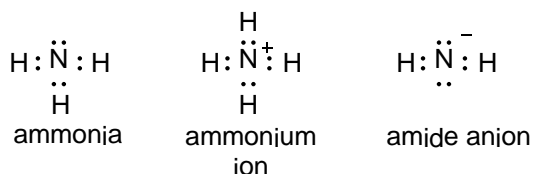
**Lewis structures** represent the valence electrons of an atom as dots. By using Lewis structures one can recognize if any atoms possess lone-pair electrons or have a formal charge. For example, water and hydroxide ion can be represented by Lewis structures as shown below.



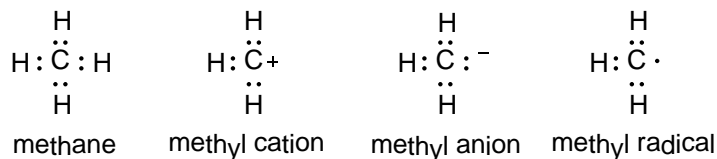
Valence electrons not used in bonding are called nonbonding electrons or lone-pair electrons. A positive or a negative charge assigned to an atom is called a formal charge; water molecule has no formal charge but the oxygen atom in the hydroxide ion has a formal charge of -1.

$$\text{formal charge} = \text{number of valence electrons} - \left( \text{number of lone-pair electrons} + \frac{\text{number of bonding electrons}}{2} \right)$$

Nitrogen has five valence electrons and the Lewis structures of ammonia, ammonium ion, and amide anion are shown below. Ammonium ion has a formal charge of +1 and amide anion has a formal charge of -1.

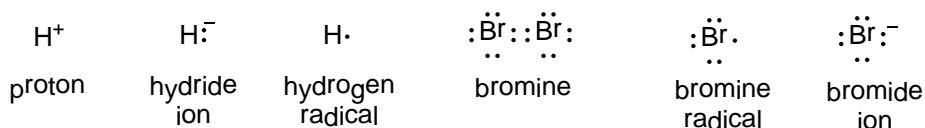


Carbon has four valence electrons and the Lewis structures of methane, methyl cation, methyl anion, and methyl radical are shown below.

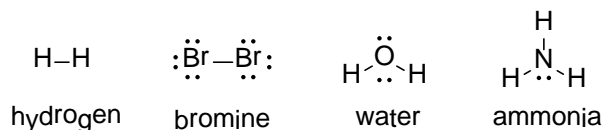


A species containing a positively charged carbon atom is called a **carbocation**, and a species containing a negatively charged carbon atom is called a **carbanion**. A species containing an atom with a single unpaired electron is called a **radical** or a **free radical**.

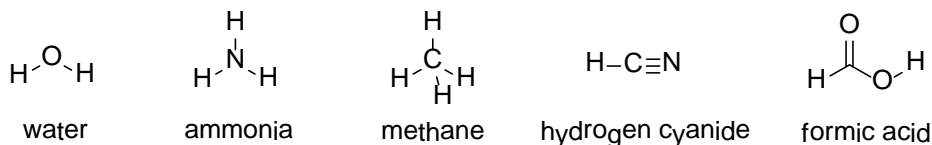
Hydrogen has one valence electron and each halogen (F, Cl, Br, I) has seven valence electrons, so the following species have the indicated formal charges:



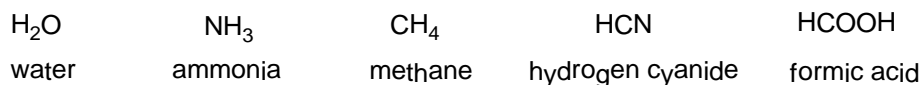
A pair of shared electrons can also be shown as a line between two atoms. The hydrogen has one covalent bond and no lone pair. The halogens have one covalent bond and three lone pairs. The oxygen of water has two covalent bonds and two lone pairs. The nitrogen of ammonia has three covalent bonds and one lone pair. Each atom has a complete octet except hydrogen which has completely filled outer shell.



**Kekulé structures** represent the bonding electrons as lines and the lone-pair electrons are usually left out entirely, unless they are needed to draw a mechanism for a chemical reaction.



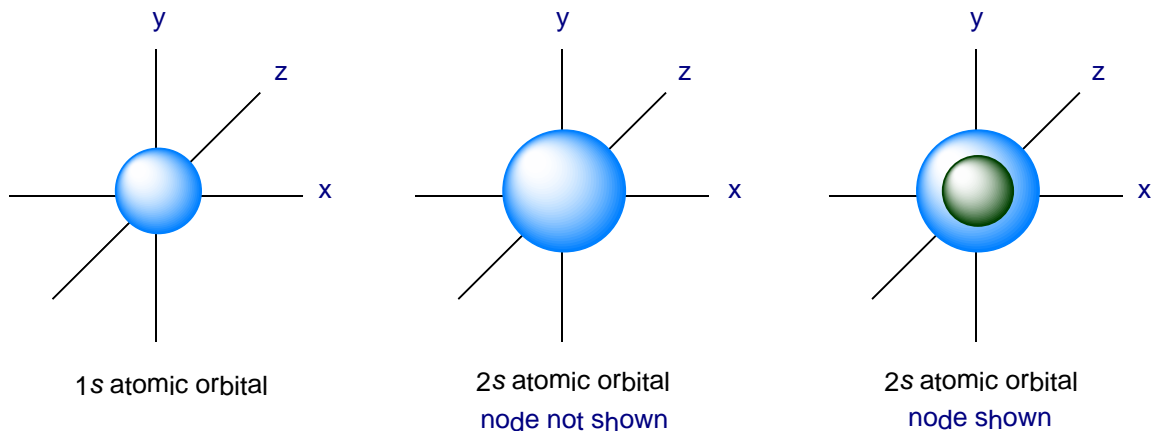
Sometimes some of the covalent bonds of the structure of a compound are omitted for simplification. These kinds of structures are called **condensed structures**.



## 1.5 Atomic Orbitals

An orbital is a three-dimensional region around the nucleus where the probability of finding an electron is high. Mathematical calculations and experimental evidence indicate that the  $s$  atomic orbital is a sphere with the nucleus at its center. According to the **Heisenberg uncertainty principle**, both the location and the momentum of an atomic particle cannot be determined simultaneously.

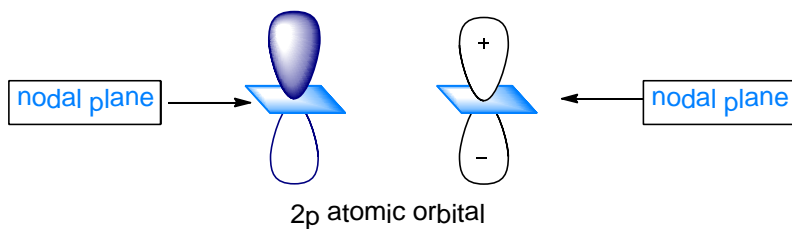
We can never say exactly where an electron is. We can only describe its probable location. If we say that an electron occupies a  $1s$  atomic orbital, it means, there is a greater than 90% probability of finding the electron in the space which is defined as the sphere for  $s$  orbital. The average distance from the nucleus is greater for an electron in a  $2s$  atomic orbital than for an electron in a  $1s$  atomic orbital. Consequently, the average electron density in a  $2s$  atomic orbital is less than the average electron density in a  $1s$  atomic orbital. An electron in a  $1s$  atomic orbital can be anywhere within the  $1s$  sphere, but there is a node in a  $2s$  atomic orbital where the probability of finding an electron is zero.



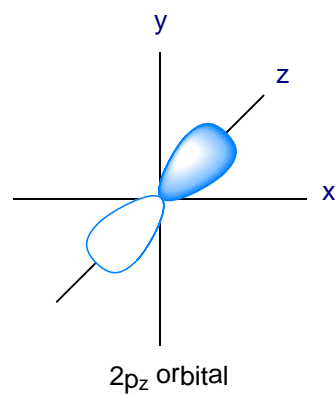
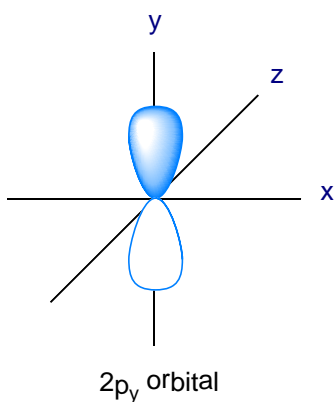
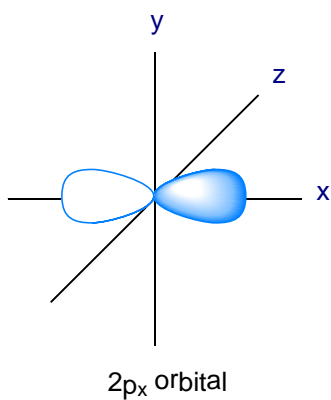
Unlike  $s$  atomic orbitals,  $p$  atomic orbitals have two lobes which are of opposite phase. These two phases can be designated by plus and minus signs.

A plane that passes through the center of the nucleus of the  $p$  atomic orbital is called, nodal plane that bisects the two lobes. There is zero probability of finding an electron in the nodal plane of the  $p$  orbital.





We have seen that there are three degenerate  $p$  atomic orbitals. The  $p_x$  orbital is symmetrical about the  $x$ -axis,  $p_y$  the orbital is symmetrical about the  $y$ -axis, and  $p_z$  the orbital is symmetrical about the  $z$ -axis. All these  $p$  orbitals are perpendicular to each other. The energy of a  $2p$  atomic orbital is slightly greater than that of a  $2s$  atomic orbital.

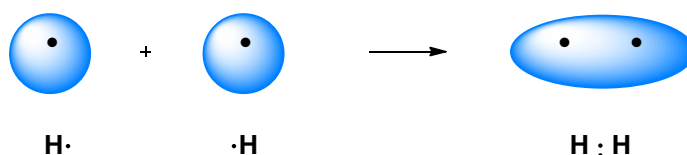


# Module 1 Electronic Structure and Covalent Bonding

## Lecture 2 Structure and Bonding II

### 1.6 Molecular Orbital Theory

According to molecular orbital theory, covalent bonds result from the combination of two atomic orbitals to form molecular orbitals. For example, in hydrogen molecule the 1s atomic orbital of one hydrogen atom overlaps with the 1s atomic orbital of a second hydrogen atom to give a molecular orbital. The covalent bond that is formed when the two s atomic orbitals overlap is called a cylindrically symmetrical  $\sigma$ -bond.



- During bond formation, energy is released as the two orbitals start to overlap. More energy released as increases the overlap of orbitals. When the atoms approach each other, their positively charged nuclei repel each other. This repulsion causes a large increase in

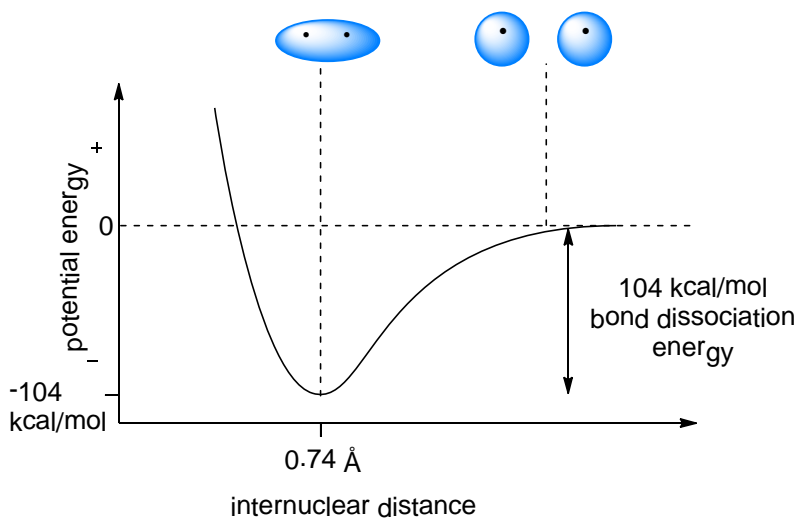


Figure 1

energy. We see that maximum stability is achieved when the nuclei are a certain distance apart. This distance is the bond length of the covalent bond which is 0.74 Å for hydrogen molecule (Figure 1). When the bond forms, 104 kcal/mol of

energy is released and the same amount of energy has to be given for breaking the bond. The energy required to break a bond is called the **bond dissociation energy**.

- Atomic orbitals can combine in two different ways. For example, the  $1s$  orbitals of two hydrogen atoms approach each other and combine constructively, when they are in phase and have the same sign, to give a  $\sigma$  bonding molecular orbital (Figure 2).

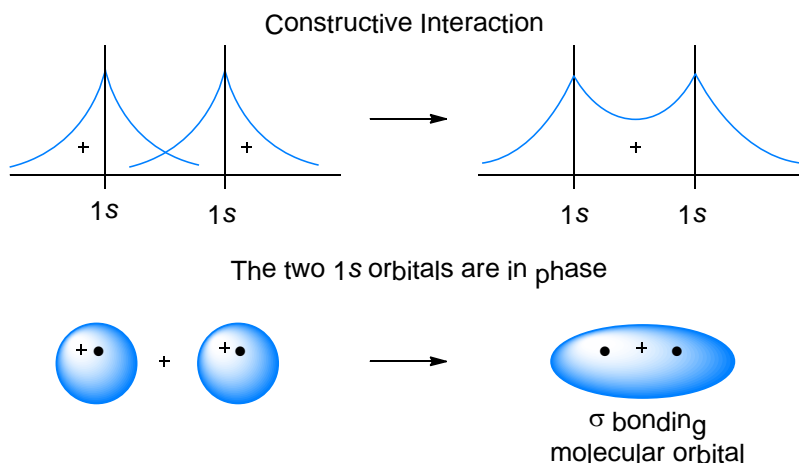


Figure 2

- When two hydrogen  $1s$  orbitals overlap out of phase with each other, an  $\sigma^*$  antibonding molecular orbital results. When the two  $1s$  orbitals have opposite signs, they tend to cancel out where they overlap. The result is a node that separates the two atoms (Figure 3).
- The relative energies of the atomic orbitals and the molecular orbitals of the system are shown in the molecular orbital diagram (Figure 4). In the MO diagram, the energies are represented as horizontal lines; the bottom line is the lowest energy level, the top line the highest energy level. When the  $1s$  orbitals are in phase, the resulting molecular orbital is an  $\sigma$ -bonding molecular orbital which is lower in energy than that of a  $1s$  atomic orbital.

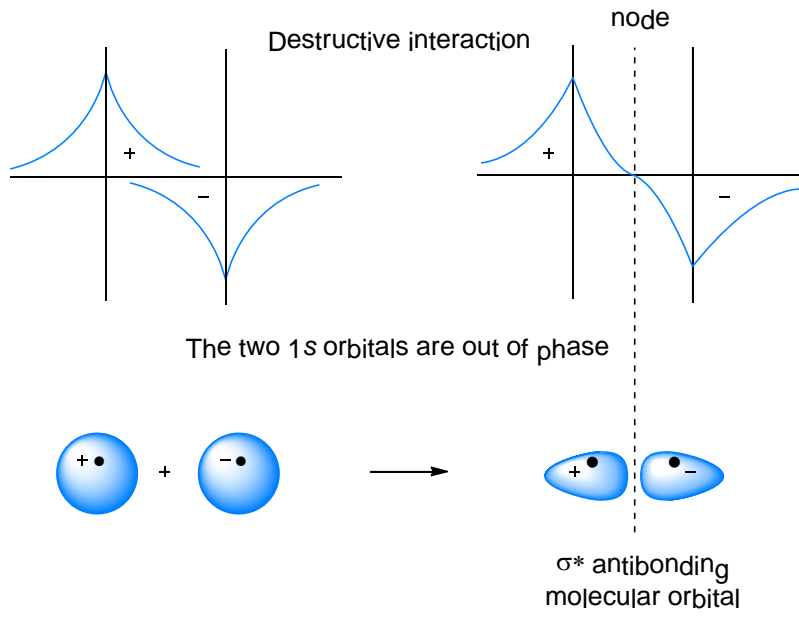


Figure 3

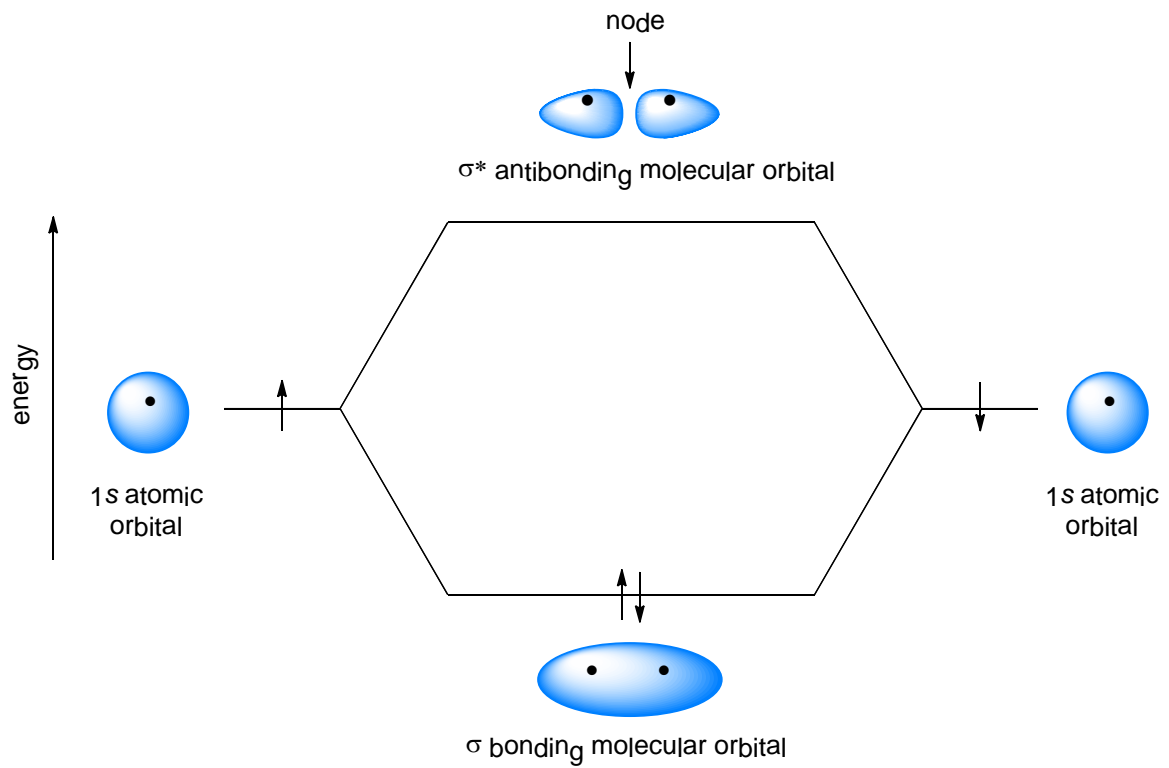


Figure 4

- When two  $1s$  orbitals overlap out of phase, they form an antibonding orbital which is higher in energy than that of a  $1s$  atomic orbital. After the MO diagram is constructed, the electrons are assigned to the molecular orbitals according to the *Aufbau Principle* and the *Pauli Exclusion Principle* which state that electrons always occupy available the lower energy orbitals and no more than two electrons can occupy one molecular orbital.
- We can also predict whether a compound is stable to exist. For example, helium would have four electrons. Two of them can be filled in the lower energy bonding molecular orbital and the remaining two can be filled in the higher energy antibonding molecular orbital. The two electrons in the antibonding molecular orbital would cancel the advantage to bonding gained by the two electrons in the bonding molecular orbital.
- Two  $p$  atomic orbitals can overlap either end-on or side-to-side (Figure 5). First, let us consider end-on overlap. If the overlapping lobes of the  $p$  orbitals are in-phase, an  $\sigma$  bonding molecular orbital is formed. The electron density of the bonding molecular orbital is concentrated between the nuclei, which causes the back lobes of the molecular orbital to be quite small. The bonding molecular orbital has two nodes.
- If the overlapping lobes of the  $p$  orbitals are out-of-phase, an  $\sigma^*$  antibonding molecular orbital is formed. The antibonding molecular orbital has three nodes.
- Side-to-side overlap of two  $p$  atomic orbitals forms a  $\pi$ -bond (Figure 6). Side-to-side overlap of two in-phase  $p$  atomic orbitals forms a  $\pi$  bonding molecular orbital, whereas side-to-side overlap of two out-of-phase  $p$  orbitals forms an  $\pi^*$  antibonding molecular orbital.
- The bonding molecular orbital has one nodal plane that passes through both nuclei. The antibonding molecular orbital has two nodal planes.
- The bond formed by the end-on overlap of  $p$  orbitals is stronger than a bond formed by the side-to-side overlap of  $p$  orbitals. So an  $\sigma$  bonding molecular orbital is more stable than a  $\pi$  bonding molecular orbital.

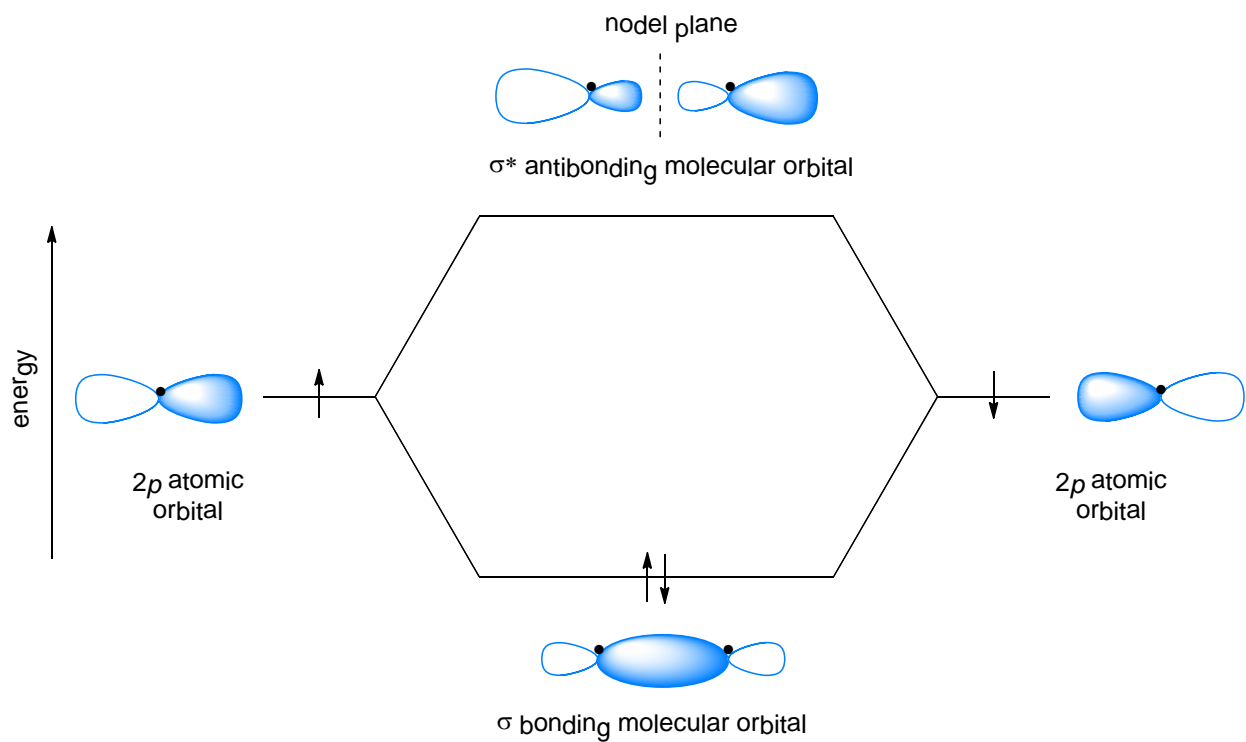


Figure 5

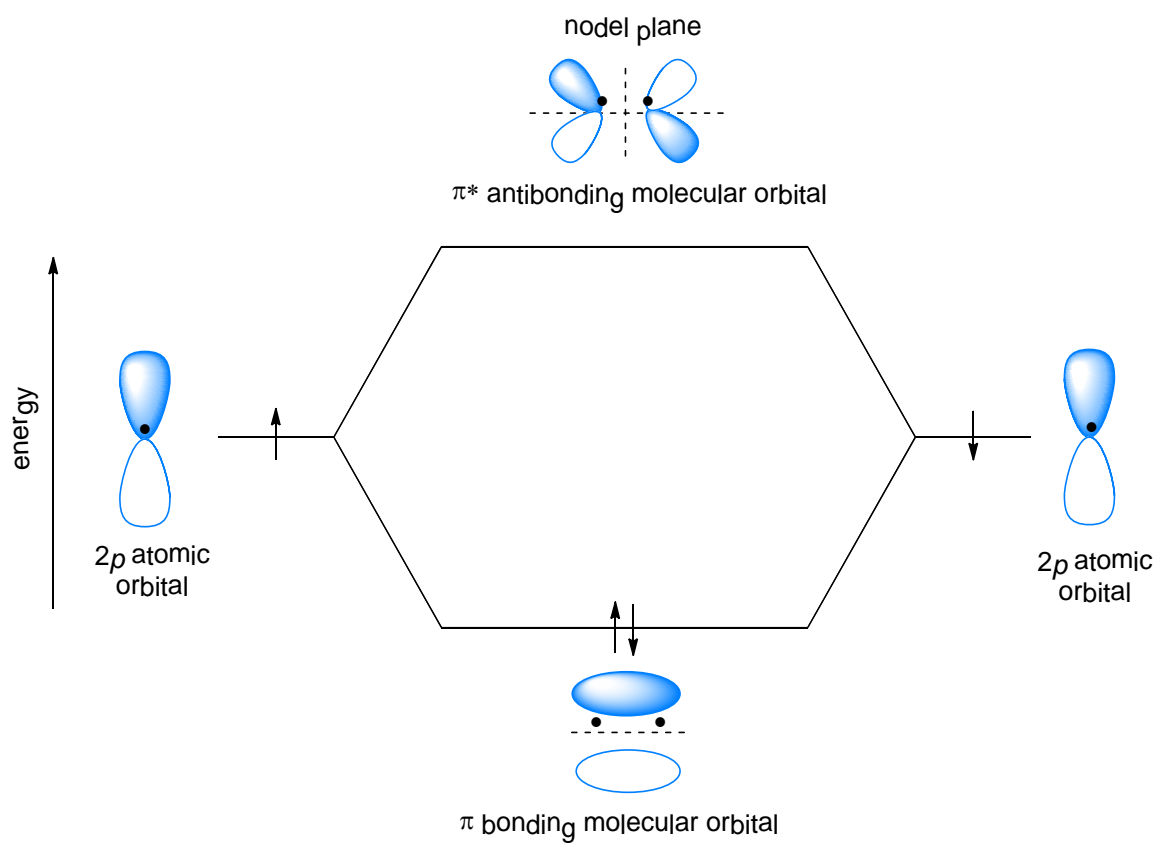


Figure 6

## 1.7 Hybridization and Molecular Shapes

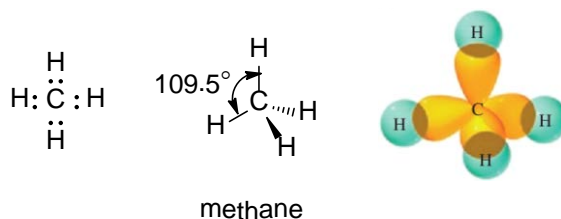
If we consider the bond angles of organic molecules using  $s$  and  $p$  orbitals, we expect bond angles of about  $90^\circ$  because  $s$  orbitals are nondirectional, and the  $p$  orbitals are oriented at  $90^\circ$  to one another. But experimental evidence shows, however, that bond angles in most of organic compounds are close to  $109^\circ$ ,  $120^\circ$  or  $180^\circ$ .

According to *valence-shell electron-pair repulsion theory* (VSEPR theory), the bonds pair and the lone pair electrons repel each other and attain the largest possible angles. An angle of  $109.5^\circ$  is the largest possible separation for four pairs of electrons,  $120^\circ$  is the largest separation for three pairs, and  $180^\circ$  is the largest separation for two pairs.

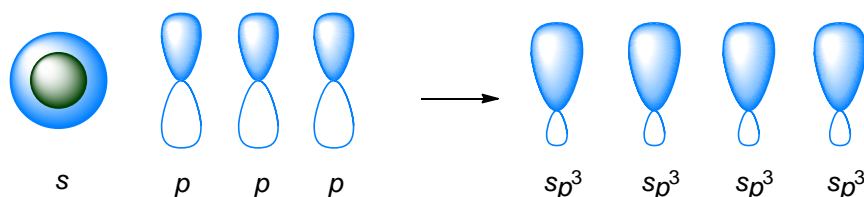
To explain the shapes of common organic molecules, we assume that the  $s$  and  $p$  orbitals combine to form hybrid orbitals that separate the electron pairs more widely in space. Hybrid orbitals are mixed orbitals that they result from combining orbitals. The concept of combining orbitals is called hybridization.

### 1.7.1 $sp^3$ Hybrid Orbitals

Methane is the simplest example of  $sp^3$  hybridization. Methane has four covalent bonds with same length. The bond angles of all the covalent bonds are same ( $109.5^\circ$ ) which gives a tetrahedron shape. So the four bonds in methane are identical.

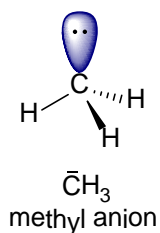


These four degenerate orbitals are called  $sp^3$  hybrid orbitals formed by the combination of one  $s$  orbital and three  $p$  orbitals. Each orbital has 25%  $s$  character and 75%  $p$  character.



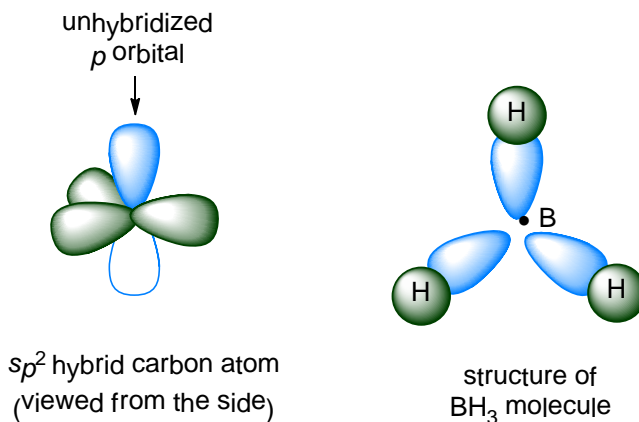
A  $sp^3$  orbital has two lobes with different size because the  $s$  orbital adds to one lobe of the  $p$  orbital and subtracts from the other lobe of the  $p$  orbital. The larger lobe of the orbital is used in covalent bond formation. The four orbitals arrange themselves as far away as possible in space to minimize the repulsion. They point toward the corners of a regular tetrahedron.

The negatively charged carbon in the methyl anion has three pairs of bonding electrons and one lone pair. The four pairs of electrons, three bond pair and two electrons, point toward the corners of a tetrahedron. In the methyl anion, three of carbon's  $sp^3$  orbitals overlap with the  $s$  orbital of a hydrogen and forms covalent bonds, and the fourth  $sp^3$  orbital holds the lone pair.



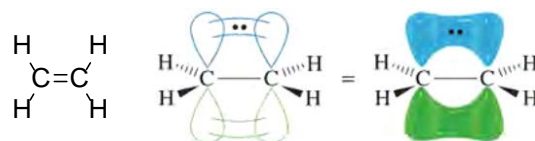
### 1.7.2 $sp^2$ Hybrid Orbitals

When an  $s$  orbital combines with two  $p$  orbitals, three hybrid orbitals results that are oriented at  $120^\circ$  angles to each other. These orbitals are called  $sp^2$  hybrid orbitals. The remaining unhybridized  $p$  orbital perpendicular to the plane of the three  $sp^2$  hybrid orbitals. The  $120^\circ$  arrangement is called trigonal geometry.

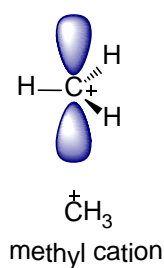




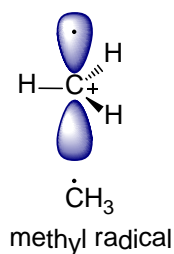
For example, each carbon atom of ethene has three  $sp^2$  hybridized orbital and one unhybridized  $p$  orbital. The  $sp^2$  hybridized orbital of each carbon atom forms two  $\sigma$ -bonds by overlapping with  $s$  orbitals of two hydrogens and one  $\sigma$ -bond by overlapping with  $sp^2$  orbital of the other carbon atom. The sidewise overlap of the unhybridized  $p$  orbital of each carbon atom gives a  $\pi$ -bond.



The positively charged carbon in the methyl cation is  $sp^2$  hybridized. It forms three covalent bonds using  $sp^2$  orbitals by overlapping with  $s$  orbital of hydrogen atom. Its unhybridized  $p$  orbital stands perpendicular to the plane and remains empty.



The carbon atom in the methyl radical is also  $sp^2$  hybridized. The methyl radical has one unpaired electron. That electron is in the unhybridized  $p$  orbital.



### 1.7.3 $sp$ Hybrid Orbitals

When an  $s$  orbital and a  $p$  orbital of an atom combine, a  $sp$  hybridized orbital is formed. For example, each carbon atom of ethyne has one  $sp$  hybridized orbital and two unhybridized  $p$  orbitals. The two unhybridized  $p$  orbitals are perpendicular to each other. One end of the  $sp$  hybridized orbital overlap with  $s$  orbital of hydrogen and the other end overlap with  $sp$  hybridized orbital of the other carbon atom. Sidewise overlap of two unhybridized  $p$  orbitals gives a  $\pi$ -bond. So ethyne molecule has one  $\sigma$ -bond and two  $\pi$ -bonds. These hybrid orbitals give a bond angle of  $180^\circ$  that leads to linear arrangement.

